Investigation of PTFE Transfer Films by Infrared Emission Spectroscopy and Phase-Locked Ellipsometry

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SUMMARY

When a PTFE sheet was rubbed unidirectionally over a smooth surface of stainless steel, an essentially monomolecular transfer film was formed. By ellipsometric and emission infrared spectroscopic techniques it was shown that the film was 10-15 Å thick and birefringent. From the intensity differences of infrared bands obtained with a polarizer passing radiation polarized in mutually perpendicular planes, it was possible to deduce transfer film orientation with the direction of rubbing.

After standing in air for several weeks the transfer films apparently increased in thickness by as much as threefold. At the same time both the index of refraction and the absorption index decreased. Examination of the surfaces by optical and electron microscopies showed that the films had become porous and flaky.

These observations were consistent with previous tribological measurements. The coefficients of friction decreased with the formation of the transfer film but increased again as the film developed breaks.

The applicability of the ellipsometric and polarized infrared emission techniques to the identification of monomolecular tribological transfer films of polymers such as PTFE has been demonstrated.

INTRODUCTION

There is ample evidence that the frictional properties of polytetrafluoroethylene (PTFE) depend on the development of a transfer film of PTFE on the material against which it rubs. Pooley and Tabor (ref. 1) and Makinson and Tabor (ref. 2) have shown that in air at low speeds (approximately 1 mm/sec) the transferred material consisted of lumps initially, but that it changed into sheets or streaks after sliding for some time. This film was estimated to have been less than 10 nm thick. At higher speeds (>100 mm/sec) the transfer film always contained fragments.

Pepper (ref. 3) studied the transfer of PTFE to S-Monel under high vacuum by Auger electron spectroscopy (AES). From the attenuation by the film of

Auger electrons from the substrate he estimated that the film was two to four molecules thick.

Wheeler (ref. 4) prepared transfer films by sliding a high purity high density PTFE rod on pure nickel and S-Monel in high vacuum. The transfer film was examined by x-ray photoelectron spectroscopy and found to be indistinguishable from bulk PTFE. A trace of metal fluoride was also observed.

Briscoe (ref. 5) considered the transfer of PTFE as one of "cold, total transfer." He differentiated it from "hot, total transfer," such as is observed for polymethyl methacrylate (PMMA) in which melting occurs and from "degraded transfer," which is observed in highly cross-linked systems, such as rubbers and resins. As a result of its mode of transfer, the PTFE transfer film is highly oriented but does not adhere strongly to the smooth surfaces on which it is formed. Thus when a PTFE pin was made to slide slowly and repeatedly on a smooth solid surface, the coefficient of friction, initially high, decreased to a constant low value, but significantly increased again when the pin was turned through 90°. Briscoe (ref. 6) explained this behavior in terms of a lumpy transfer film which became oriented but then became lumpy again when the pin was turned. When the surface was rough or sliding speed fast, the friction remained high because, Briscoe deduced, the lumpy transfer film was not allowed to "stretch out" or become oriented.

The objective of this work was to demonstrate the formation of an oriented PTFE transfer film on steel in air, to determine its thickness, and to examine its stability over a period of time. Techniques used were polarized Fourier infrared emission spectrophotometry and phase-locked electronic ellipsometry.

EXPERIMENTAL

Infrared Emission Accessory

Figure 1 shows the accessory in perspective (top) and the method of its interfacing with a commercial Fourier (Nicolet, Model MX-1) spectrophotometer (bottom). The accessory was built by Harrick Scientific Corporation. It was mounted on a bracket placed on the outside of the spectrometer case at a height such that the radiation from the sample surface was brought into the optical plane, 5 cm (2 in.) above the base plate of the spectrophotometer. An optical microscope is part of the attachment. It permits not only the viewing of the sample area whose spectrum is to be determined, but it also functions as a reference for alignment. Below the microscope is the stage holding the heated sample insert under a cold heat shield. The stage can be horizontally tilted with respect to the microscope axis at angles up to 60° and the sample insert within the stage can be moved in the x,y directions (in the plane of the stage) and in the z-direction (normal to the plane of the stage). As shown in the schematic drawing of figure 1, a cartridge heater can heat the sample insert, a 0.95 cm (3/8 in.) diameter stainless steel disc of 0.16 cm (1/16 in.) thickness, from the bottom through the "dome," the metal (stainless steel) holder. A thermocouple in the dome allows the temperature to be read at a position in the dome just below the insert. The cold shield, a highly polished cover over the dome, separately supported so as to make contact with the dome only through an insulating porcelain ring, holds a polished aluminum mask in its center. Masks of different hole size are furnished to limit the sample surface area

2

viewed. These "cold" masks are very important to the functioning of the accessory; they greatly reduce stray thermal radiation.

The sample surface, which can be heated to and thermostatted at temperatures up to 300 °C, is located in one focal plane of the 90° off-center elliptical mirror. An area as small as 1 mm in diameter at the focus in the sample plane can be analyzed. An enlarged image (10 X) is formed at the other focus of the elliptical mirror. The microscope (shown as an "eye") on top of the accessory allows viewing the sample through a hole in the elliptical mirror. As shown, the radiation emitted by the sample and reflected 90° by the elliptical mirror is brought to a focus at the same distance from a plane mirror as the original hot source supplied by the spectrometer. Therefore the radiation from the surface of the insert replaces the radiation of the spectrometer source. The only changes--easily reversible--that had to be made to the spectrometer, were a hole in the case, which could be covered when not needed, and the insertion of the flat mirror into the optical path between instrument source and collimator.

When the emission accessory was used no (absorbing) sample was placed in the sample compartment of the spectrometer. However, for polarization spectroscopy, an infrared filter (parallel wires, 0.4 μm thick and separated by 0.4 μm from one another, of aluminum deposited on KRS-5) was placed in the focal plane of the sample compartment. This filter could be rotated in its plane--equivalent to the sample surface of the insert--to effectively transmit only sample radiation polarized along or perpendicular to a preferred direction in the sample plane.

The reproducibility of emission spectra obtained with this accessory was better than 1 percent for 1000 accumulated and averaged spectra (the instrument recorded 1 spectrum/sec for a resolution of 1 cm^{-1}).

Faraday Effect-Modulated Ellipsometer

Since this instrument and its operation were described in a previous publication (ref. 7), only a few remarks are necessary here. Ellipsometry measures the change in the polarization state of a beam of light when it is reflected from a surface. Two incident beams orthogonally polarized give two reflected beams of different polarization states, from which two variables can be calculated: the refractive index (n) and the absorption index (k) of the surface. When the surface is coated by a very thin layer of material, the reflected radiation is composed of radiation reflected at the front surface and radiation reflected at the back surface and transmitted through the layer. Additional variables- the thickness of the layer (t) and its refractive and absorption indices--are introduced. In principle, all of these variables can be determined by ellipsometry if, for example, three known angles of incidence are used in three separate measurements. The total number of variables is five (n and k for both the film and the substrate and t for the film) so that one variable would be overdetermined and could be used to find the best fit. In practice, the errors of measurement are too great to allow the solution of six equations simultaneously, especially since these equations are nonlinear. Different mathematical models can be adopted, e.g. one can insert all the predetermined constants of the pure materials into the equations or one can solve for all or some of the unknowns from measured values at a number of angles.

3

The latter procedure takes care of the observation that even the same surface of a given material is never really homogeneous because of stresses and chemical reactions. One must remember that ellipsometry is sensitive even to fractions of monolayers. These remarks will tell the reader that a computer program allowing many model variations, checks, and cross-checks is very important.

As will be shown later, the orientation of the PTFE film, manifesting itself by different refractive indices in different directions, i.e. by double refraction, caused further complexity. The model that resulted in the same layer thickness in two perpendicular viewing directions, using the different indices for these directions, was taken to be the best one. Conversely, the convergence of results for film thickness with different optical constants derived from measurements along different directions on the sample surface was a good indication of the birefringence and hence the orientation of the PTFE film.

Sample Preparation

The 304 stainless steel inserts 0.95 cm diameter disks, were, in sequence, cut off from bar stock, deburred, abraded with silicon carbide paper up to 600 grit size, polished with jeweler's rouge, ultrasonically cleaned with distilled water and soap and, finally, washed with methanol. The PTFE used was a sheet 2.5 by 16 by 0.16 cm (1 by 6 by 1/16 in.) in dimensions. It was prerubbed against an insert until smooth, then rubbed against the sample insert in one direction only under 100 to 200 g (one finger) pressure. Single 5-in. strokes, double 5-in. strokes and five 0.5-in. strokes were applied to various samples at speeds varying between 0.1 and 5 sec per stroke, but averaging 1.0 sec per stroke.

RESULTS

Ellipsometric Measurements Applied to Differently Prepared Samples

Initially some samples were prepared by rubbing PTFE sheet on the metal in random directions. Ellipsometry of these samples invariably failed to show any transfer film. Similarly attempts to transfer PTFE to gold-plated inserts failed. Unidirectional application of PTFE to stainless steel, as described in the preceding section, did work in that PTFE was transferred to the metal. No correlation was found between the amount of PTFE transferred (film thickness) and sliding speed, but a positive correlation was found between PTFE transferred and sliding distance.

Two models were finally used for the ellipsometric data conversions. In both models the observed values of the refractive and absorption indices of the stainless steel substrate were inserted. However, in the first model, the literature values of n and k for PTFE (n = 1.35, k = 0) were introduced and the computer program calculated n, k, and t for the transfer film.

Table I gives the optical constants determined ellipsometrically for the steel inserts before and after rubbing against a sheet of PTFE. In all three cases listed, both n and k were lower after rubbing than before, indicating a

coating of PTFE. The optical constants of Sample No. 6 showed a further decrease when the measurements were repeated two months later.

The results of the calculations of the optical constants according to the two models, i.e. (a) literature values for the optical constants of PTFE versus (b) values calculated from the measured data, are shown in Table II. The fits are equal or better for Model (b). Here too the optical constants of Sample No. 6 were found to be lower from measurements made two months later. The layer thickness of Sample 6 appeared to increase threefold in two months.

Table III shows the effect of sample orientation on the calculated ellipsometric data. The reason for the large discrepancy between the results of Sample No. 5 is unknown. The differences for the other samples are more reasonable. A lower index of refraction and of absorption for PTFE in a direction perpendicular to the direction of sliding is in line with the birefringence of PTFE transfer film observed by other workers (ref. 1). Since a monomolecular layer of PTFE is typically only about ten Angstroms thick, Sample No. 7 was coated with the thinnest possible continuous film and it was definitely birefringent.

The effect of age of Sample No. 6 was remarkable. It was not a coincidence, for another similar sample (No. 9) prepared on August 5, 1986, had initial values for n, k, and t of 1.45, 2.24, and 9.6 Å and corresponding values on September 11, 1986 of 1.14, 2.16, and 44.3 Å. In other words, the film thickness appeared to increase three to four-fold and the optical constants dropped considerably.

The riddle was solved when we looked at the sample under the electron microscope (fig. 2). Clearly, the film had partly peeled off the substrate, giving rise to an effectively-air-diluted film of greater thickness and lower optical constants.

Infrared Emission Spectra of PTFE on Stainless Steel

The thinnest transfer film of PTFE, which was well characterized by ellipsometry, was Sample No. 7. Its birefringence was already established (table I). Although infrared emission spectra were obtained on other samples as well, all the transfer film spectra included here will refer to this sample since it will best illustrate the transfer of PTFE to steel.

The study of the transfer of PTFE by infrared emission is aided by: (1) the great intensity of the infrared bands corresponding to the C-F stretching vibration, and (2) the high melting point of PTFE, making it possible to obtain emission spectra at 250 to 260 °C, which was the temperature used in this work. These factors gave us strong spectra of layers as thin as monomolecular (<10 Å). The most intense bands occur in the 950 to 1350 cm^{-1} infrared region; hence the spectra shown below will be limited to that region.

Figure 3 shows, for comparison, an emission spectrum of the bulk PTFE sheet that was used for rubbing. It is an emission spectrum though the bands are pointing downward as they would in an absorption spectrum. The reasons for the band inversion, in this case, is the great thickness of the absorbing

sample, the reflection of emitted radiation at the PTFE/air interface, and the anomalous dispersion of the index of refraction, which is responsible for the reflection, over the region of very strong absorption bands. The theory behind the band inversion was described by Hvistendahl et al. (ref. 8). It was noted that the main band peaks have frequencies of 1150, 1215, 1242, 1298, and 1341 cm^{-1}. These bands are marked on the spectra. Here, as in the following spectra, the ordinate is the percentage emission of the sample compared to that of a blackbody in the same configuration and at the same temperature. Fine graphite powder smeared on a similar insert and recorded in the same way was used as blackbody.

The emission spectra of the sample disks coated with the PTFE transfer films on the stainless steel inserts were also inverted PTFE spectra primarily because the emission from the substrate was strong enough to pass through the very thin transfer film. Therefore the emissivities (percentages of sample emission to blackbody emission) of the coated inserts were less than those of the blanks. However, because of the small absorption, these spectra showed very little contrast, so little that the presence of the PTFE was sometimes difficult to see. Fortunately, polarization of the radiation absorbed by the PTFE film discriminated against the unpolarized background radiation from the steel. The polarizing filter can therefore be considered an almost indispensible tool for the proper recording of infrared emission spectra of very thin--monomolecular or near-monomolecular--surface layers. Since such layers are generally ordered structures, their infrared emissions or absorptions are almost always polarized.

Figure 4 shows an emission spectrum of Sample No. 7 on the stainless steel insert. Only one strong (absorption) peak at approximately 1250 cm^{-1} is noticeable and there is a shoulder at approximately 1149 cm^{-1}. The insert was located in a horizontal plane (normal to the microscope axis of the accessory (fig. 1)). The polarizer was turned that only radiation polarized in a direction normal to the rubbing direction (of the PTFE on the steel) was passed to the detector. Figure 5 shows the corresponding spectrum of the uncoated blank. The ordinates are percentages of equivalent blackbody emissions which, in agreement with our previous statements, are clearly higher for the uncoated than for the coated insert surfaces.

The spectrum of figure 6 was obtained after turning the sample by 90° in its plane. Now the band peaking at 1149 cm^{-1} is more intense than the 1250 cm^{-1} band.

Turning the sample in its plane should be equivalent to turning the polarizer by the same angle. Figure 7 shows that this prediction turned out to be nearly true; the small differences are probably ascribable to the guesswork involved in turning the sample through 90°.

As noted earlier, these spectra were not easily obtained; they required the co-adding of at least 1000 spectra and the highest possible resolution to permit a high degree of smoothing.

DISCUSSION

PTFE has a helical structure containing difluoromethylene units (CF_2) along the chain and exists as a largely crystalline material in the solid state. Two solid state transitions at approximately 30 and 19 °C have been observed, but their nature is still under discussion. It is, however, generally agreed (ref. 9) that between 19 and 30 °C, the PTFE polymer chain has a helical configuration in which 15 CF_2 groups are arranged in seven turns of the helix (a 15_7 helix). Above 30 °C the conformation may become more irregular, although the hexgonal arrangement of chains is maintained. Such a conformationally disordered (Boltzmann-distributed) chain would have the 1149 and 1250 cm^{-1} bands of about equal intensity as in figure 7 while the 15_7 helix would have the 1250 cm^{-1} band almost twice as strong as the 1149 cm^{-1} band. Both of these bands were assigned to the E_1 mode of vibration in the four most likely helical models. The transition dipole moment vectors for both of these vibrations are perpendicular to the molecular axis and at an angle to each other. Clearly rubbing the insert surface with PTFE produces a film that is oriented since the intensities of the corresponding infrared bands vary with orientation. If more band intensity changes were observable, it would, in principle, be possible to determine the exact orientation of PTFE film with respect to the substrate surface and the direction of rubbing. The infrared spectra are threfore consistent with the ellipsometer data in showing birefringence of the transfer film.

The demonstrated generation of these transfer films in air and their orientation with respect to the sliding direction can explain the observations of Briscoe and others (ref. 6) with regard to friction and wear, to which reference was made in the Introduction. However, the observation of the "Peeling Off Effect" (fig. 2) was apparently not described previously. It would explain the lack of orientation of PTFE films and increased wear after aging.

This work therefore contributed to proving the usefulness of ellipsometry and of (primarily polarized) infrared emission spectroscopy to surface analysis in tribology.

ACKNOWLEDGMENT

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TABLE I. - OPTICAL CONSTANTS FOR 304-STAINLESS STEEL
INSERTS BEFORE AND AFTER RUBBING AGAINST PTFE

Sample number	Sliding distance, cm	n		k	
		Before	After	Before	After
5	25	2.63	2.16	3.62	3.34
6 (on 7/15/86)	12	2.12	1.87	3.50	3.34
(on 9/20/86)		----	1.31	----	2.54
7	6	2.30	2.23	3.55	3.50

NOTE: 1. The fit varied between 0.11 and 0.13.
2. Homogeneous composition (no fiber layer, just surface change was assumed).
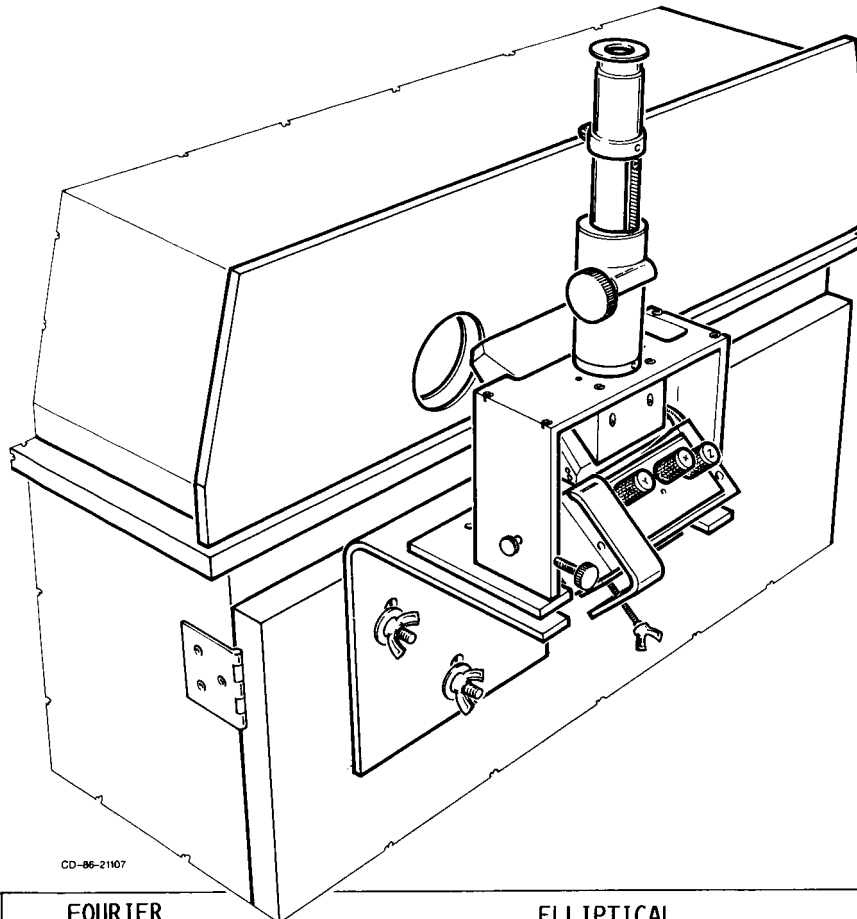3. Rubbing pressure was between 100 and 200 g (finger pressure).

TABLE II - OPTICAL CONSTANTS AND THICKNESS OF TRANSFERRED
PTFE FILM CALCULATED BY TWO MODELS

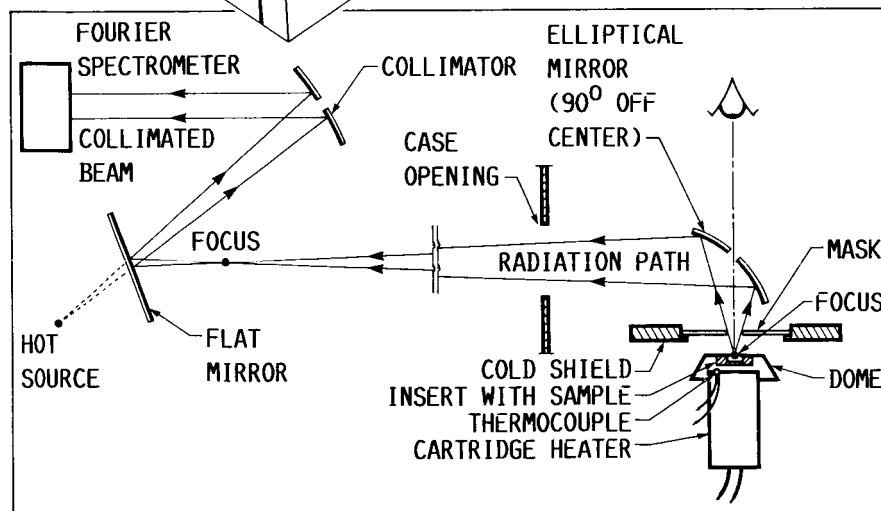| Sample number	Sliding distance, cm	t (Å) (a)	Fit (a)	n (b)	k (b)	t (Å) (b)	Fit (b)
5	25	68.0	0.32	1.79	2.41	61.1	0.27
6 (on 7/15/86)	12	44.0	.32	1.62	2.76	53.6	.28
(on 9/10/86)		----	----	1.10	1.25	149.0	----
7	6	10.8	.34	1.88	2.69	12.4	.34

[a]Assuming n = 1.35 and k = 0, the literature values for PTFE.
[b]Calculating n and k as well.

TABLE III. - EFFECT OF SAMPLE ORIENTATION WITH RESPECT
TO INCIDENT LIGHT

Sample number	Sliding distance, cm	n	k	t (Å)	fit
5 (parallel to sliding)	25	1.79	2.41	61.1	0.27
(perpendicular to sliding)		1.20	2.01	38.0	.26
6 (parallel)	12	1.62	2.76	53.6	.28
(perpendicular)		1.63	2.66	59.6	.33
7 (parallel)	6	1.88	2.69	12.4	.34
(perpendicular)		1.70	1.86	11.9	.28

9

CD-86-21107

FOURIER
SPECTROMETER ___ COLLIMATOR

ELLIPTICAL
MIRROR
(90° OFF
CENTER)

COLLIMATED
BEAM

CASE
OPENING

RADIATION PATH

FOCUS

MASK

FOCUS

HOT
SOURCE

FLAT
MIRROR

COLD SHIELD
INSERT WITH SAMPLE
THERMOCOUPLE
CARTRIDGE HEATER

DOME

SCHEMATIC OF OPTICAL PATH
FIGURE 1. - INFRARED EMISSION ACCESSORY.

10

FIGURE 2. - PARTIALLY PEELED-OFF PTFE COATING ON STAINLESS
STEEL (SEM PHOTO, 6000 X).

FIGURE 3. - INFRARED EMISSION SPECTRUM OF PTFE SHEET (NOT POLARIZED).

11

FIGURE 4. - INFRARED EMISSION SPECTRUM OF PTFE-COATED INSERT
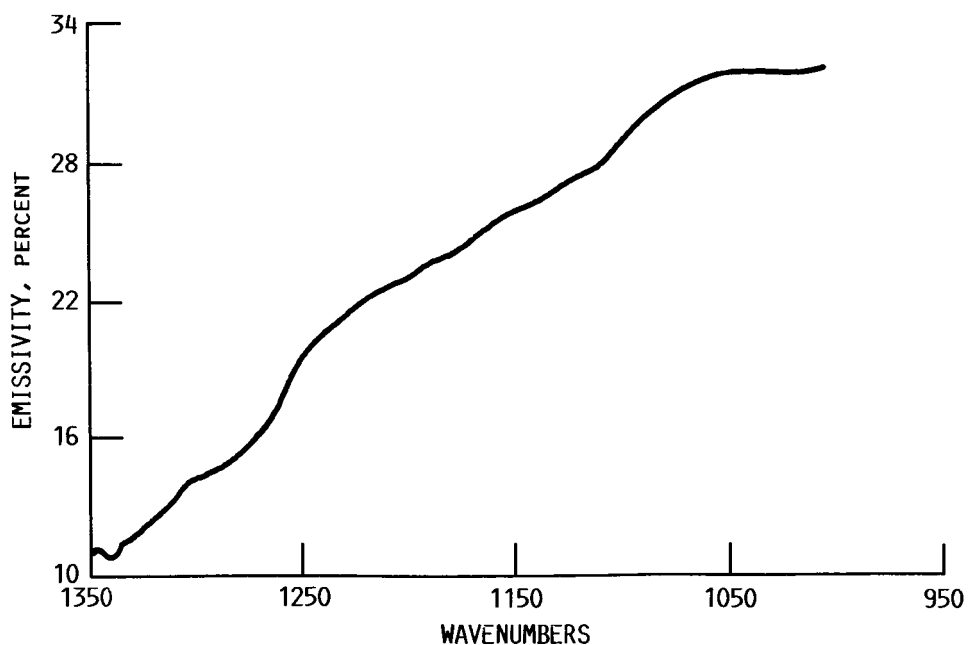(POLARIZED NORMAL TO THE STREAK DIRECTION).

FIGURE 5. - INFRARED EMISSION SPECTRUM OF BLANK INSERT (POLARIZED
IN THE SAME WAY AS FIG. 4).

12

FIGURE 6. - INFRARED EMISSION SPECTRUM OF PTFE-COATED INSERT
OBTAINED IN THE SAME WAY AS FIGURE 4 BUT WITH INSERT TURNED
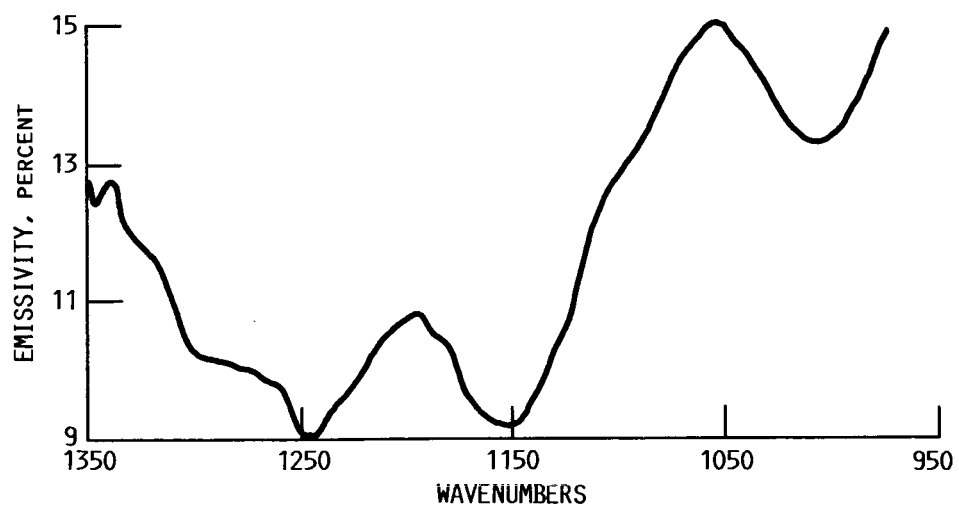90^0 IN ITS PLANE.

FIGURE 7. - INFRARED EMISSION SPECTRUM OF PTFE-COATED INSERT
(POLARIZED ALONG THE STREAK DIRECTION).

13

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16. Abstract

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